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Tunnel Effect in Widezone Crystals with Proton Conductivity

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The spectrum of thermally stimulated depolarization currents, dielectric losses, thermally stimulated luminescence, IR transmission and absorption spectra and NMR-spectra of protons in widezone hydrogen-bonded crystals had been investigated. The lines caused by protons and proton defects hesitations had been discovered in IR- spectra. In the NMR spectra revealed peaks corresponding to two non-equivalent protons. The influence of transport and tunneling of protons on the spectra of the investigated parameters is discussed. There is considered the quantum-mechanical approach to the tunneling of protons where the transparence of barrier and de Broglie wavelength had been determined.

Keywords: Proton conductors, Thermally stimulated currents, NMR and IR-spectra, Tunneling, Hydrogen bonds.

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1. INTRODUCTION

There is now growing interest to proton conductors and semiconductors, in which the main method of transport is hydrogen proton transfer. Most of the known proton conductors can be divided into three groups: high-temperature ($T > 573$ K), medium temperature $T = (573\text{-}373)$ K and low temperature $T = (373\text{-}77)$ K and below. The first and second groups of electrolytes include salts, alkaline earth zirconates, cerates and metals studied in some detail, in which the proton conductivity superprotonic phases at $T = 460$ K ranges (10^{-3}-10^{-1}) Ohm·cm^{-1}, but to date these objects found very little [1]. The third group of crystals due to the complexity of the experiment at low temperatures was studied in less details. In this regard, certainly relevant is a comprehensive study of the electrical and optical properties of these materials, the study of the mechanism of dielectric relaxation and conductivity features of proton transport and tunneling effect of interest for both basic research and development of new technologies.

It is still not created a unified theory, which predict the possibility of obtaining such materials and their behavior under extreme conditions. Wide practical application of insulating materials based on mica muscovite and phlogopite, magnesium silicate, steatite ceramics, application of lithium iodate crystals in laser technology and optical fiber communications requires more careful of their research. In operation, the laser crystals are α-$LiIO_3$ exposed powerful electromagnetic radiation, whereby they are formed, and ion radiation defects. For their study required method for determining the concentration and type of defects in laser and in electrical materials, working in conditions of radiation, for a reasonable replacement. Questions of tunneling are important in cryogenic engineering, physics of superconductors and nanotechnology, however, there is no method for determining the temperature of the tunnel effect appearance.

The aim of the investigation is to study the mechanisms of dielectric relaxation, transport, translational diffusion and proton tunneling and development of new technologies, methods of diagnosis and study of electrical and laser materials, working in harsh environments, low-temperature, high-frequency electric and magnetic fields.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Investigation of thermally stimulated depolarization currents (TSDC) of hexagonal ice crystals, magnesium hydrosilicate $Mg_3[Si_4O_{10}][OH]_2$, crystalline hydrates of calcium $CaSO_4{\cdot}2H_2O$ and copper $CuSO_4{\cdot}5H_2O$, mica muscovite $KAl_2[AlSi_3O_{10}][OH]_2$ and phlogopite $KMg_3[AlSi_3O_{10}][F,OH]_2$ and lithium iodate α-$LiIO_3$ allowed to identify all the seven peaks TSDC [1]. There had been studied crystals, calcined at various temperatures and the crystals doped with HCl and NH_4OH. It is shown that the maximum 1 TSDC is explained by relaxation of complexes $HSiO_4^{3-}$, HSO^{4-} or HIO_3, the orientation change of which is associated with proton tunnel transitions between the oxygen ions.

In the study of dielectric loss it was found three peaks $\mathrm{tg}\delta(\nu)$ in sulfates and silicates and wide one at the lithium iodate. The shift of the maxima of $\mathrm{tg}\delta$ to lower frequencies stops at temperatures below 112 K (magnesium hydrosilicate), 124 K (calcium sulfate), 175 K (lithium iodate). The relaxation time becomes independent of temperature with a very small value of the activation energy 0.03 eV, which indicates the termination of thermally activated processes and the manifestation of the tunnel effect. So there was designed "Diagnostics of tunnel effect temperature appearance in crystalline materials with proton conductivity" [2, 3].

The transmission spectra obtained with a spectrophotometer UV-ViS-NiR Cary 5000, allowed to define the band gap E_g on the intrinsic absorption edge by linear approximation of the optical transmission spectra. For lithium iodate it was found to be 4.37 eV along axis Z (C_6) and 4.46 eV along the X axis, for muscovite and phlogopite – 4.31 eV, so the studied crystals are widezone [4]. Therefore, in these crystals we can eliminate transitions of electrons from the valence band to the conduction band at low temperatures. In IR absorp-

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tion spectra obtained by the spectrometer IFS 66v / S (company BRUKER), all the lines had been identified and the IR spectra showed the presence of lines due to oscillations of protons, ions, OH^-, H_3O^+, and water molecules for silicates and lithium iodate crystals grown in H_2O (Fig. 1) and in D_2O (Fig. 2).

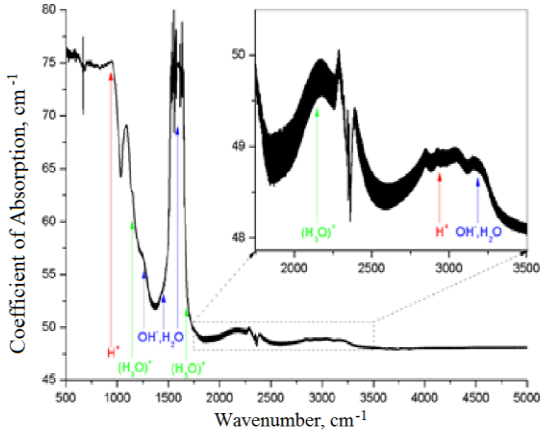

Fig. 1 – Infrared absorption spectrum α-$LiIO_3$ crystals grown in H_2O along axis Z (C_6)

From the figures it is clear that in deuterated crystals the lines 2200 cm^{-1} (H_3O^+) and 2940 cm^{-1} (H^+) are absent, that is in this crystals ions H_3O^+ and H^+ are absent and the defects D_3O are not formed. Availability of tunnel transitions with the formation of protonated ions $HSiO_4^{3-}$ (silicates) and HIO_3 (iodate) is confirmed by good agreement of activation energies in TSDC and IR spectra.

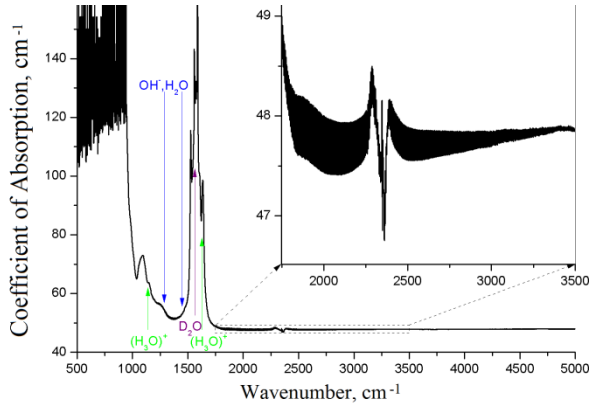

Fig. 2 – Infrared absorption spectrum of α-$LiIO_3$ crystals grown in D_2O along axis Z (C_6)

NMR spectra of protons were investigated by NMR spectrometer AVANCE IIITM 300(firm BRUKER). According to the results of NMR – spectroscopy (Table 1) by the two inclinations of $\ln\Delta\nu = f(1/T)$, where $\Delta\nu$ is the line width at half height, two ΔE_a activation energy of protons had been defined. Energy 0.056 eV coincides with the activation energy of the first maximum of the TSDC [5] due to the relaxation of anions HIO_3 and proton tunneling transitions between the oxygen ions, and the energy of 0.31 eV, which coincides with the activation energy of the maximum 3 TSDC associated with relaxation of crystalline water molecules, which is the basis for formation of proton defects H_3O^+ and OH^-.

Translational mobility of protons was determined by the formula

$$\mu = \frac{a^2 q \nu_0}{kT} \exp\left(-\frac{\Delta E_a}{kT}\right) \quad (1)$$

Here $a \approx 2$ Å – the average distance between adjacent positions in the lattice structure of protons, $\nu_0 = 2 \cdot 10^{13}\ s^{-1}$ – frequency hopping of protons, $\Delta E_a = 0.056$ eV – activation energy, while the mobility of protons is $1{,}8 \cdot 10^{-6}\ m^2/Vs$.

Table 1 – The line width of the NMR spectrum of protons in lithium iodate crystals

T, K	299	283	273	263	253	243	233	223	213
Δν, кГц	1,65 ±0,05	1,67 ±0,05	1,76 ±0,05	2,05 ±0,05	2,16 ±0,05	3,3 ±0,1	8,10 ±0,1	17,5 ±0,2	27,0 ±5

3. QUANTUM-MECHANICAL APPROACH TO THE EFFECTS OF PROTON TUNNELING

All highs of TSDC spectra are well manifested only when the polarizing field strengths are at least $1{,}5 \cdot 10^5$ V/m. This means that under such intense proton receives sufficient energy for tunneling through the potential barrier. When the thickness of the sample, for example, lithium iodate, is 0.7 mm electron would obtain the energy

$$W = \frac{qEd}{e} = \frac{1{,}6 \cdot 10^{-19} \cdot 1{,}5 \cdot 10^5 \cdot 7 \cdot 10^{-4}}{1{,}6 \cdot 0^{-19}} = 105\text{eV} \quad (2)$$

But the mass of proton is 1836,15 times more than the mass of electron, so in the same field intensity proton receives kinetic energy in 1836,15 times lower than electron, i.e. 0.057 eV. Schrödinger equation describing the motion of the proton in the periodic field of fixed nuclei allows to determine the transmission coefficient D in the form [6]

$$D = \frac{4k_1^2 k_2^{\,2}}{\left(k_1^2 + k_2^{\,2}\right)^2 sh^2 k_2 d + 4k_1^2 k_2^{\,2}}, \quad (3)$$

where

$$k_1 = \frac{\sqrt{2m_p E}}{\hbar} = \frac{2\pi}{\lambda},\ k_2 = \frac{\sqrt{2m_p (U_0 - E)}}{\hbar}. \quad (4)$$

After the transformation with a good approximation $sh^2 k_2 d = (1/4) e^{2k_2 d}$, we obtain

$$D = \left(\frac{1}{16}\left(\frac{k_1}{k_2} + \frac{k_2}{k_1}\right)^2 \cdot e^{2k_2 d} + 1\right)^{-1}. \quad (5)$$

Here for the proton at $E = 0.057$ eV, $U_0 = 0{,}07$ eV, d = 1,2 Å we obtain $D = 0.0075$. Proton with the impulse $p = k\hbar$ has an energy

$$E_n = p^2/2m_p = (k\hbar)^2/2m_p \quad (6)$$

Proton wave number $k = 2\pi/\lambda$ may be arbitrary, but discrete values, where n = 1, 2, 3, …

In this case, the energy of proton should be quantized

$$E_n = \frac{\hbar^2}{2m_p}\left(\frac{\pi}{d}\right)^2 n^2 \quad (7)$$

According to (4) the length of the de Broglie wavelength of the proton, passed the barrier, should be

$$\lambda = \frac{2\pi\hbar}{\sqrt{2m_pE}} = \frac{2\cdot 3{,}14\cdot 1{,}055\cdot 10^{-34}}{\sqrt{2\cdot 1{,}673\cdot 10^{-27}\cdot 0{,}057\cdot 1{,}6\cdot 10^{-19}}} = 1{,}2\,\text{Å}$$

On the other hand, the wavelength of de Broglie wave can be expressed as

$$\lambda = \frac{h}{m_p v} = \frac{h}{\sqrt{2m_pE_n}} = \frac{h}{\sqrt{2m_p\dfrac{\pi^2\hbar^2}{2m_pd^2}n^2}} = \frac{2d}{n}. \quad (8)$$

Energy of the proton in the ground state is

$$E_n = \frac{\pi^2\hbar^2}{2m_pd^2}n^2 = 0{,}023\text{эВ}$$

that is not contrary to the minimum amounts of energy 0.057 eV, resulting in a proton polarization.

Schrodinger equation has a physical meaning only with energies at which the width of the potential barrier is of the order of the de Broglie wavelength. That is, the width of the potential barrier for $n = 2$ must be equaled $d = n\lambda/2 = 1{,}2\,\text{Å}$, which agrees well with the distance between the oxygen ions 1,215 Å in the tetrahedron SiO_4^{4-} or between oxygen ions in SiO_4^{4-} and water molecule 1,35 Å.

4. CONCLUSIONS

Thus, a comprehensive study of a number of widezone hydrogen-bonded crystals allowed to prove the existence of the quantum tunneling effect of protons through the potential barrier at low temperatures and to develop diagnostics for his appearance temperature by TSDC spectra, tg$\delta(\nu, T)$, confirmed by IR and NMR spectra.

REFERENCES

1. V.M. Timokhin, *Appl. Phys.* No 1, 12 (2012).
2. V.M. Timokhin, Patent № 2347216 Russian Federation IPC G 01N 27/00, G 01N 25/00. Appl. 09.01.2007; Publ. 20.02.2009, Bull. No 5.
3. V.M. Timokhin, Patent № 2360239 Russian Federation IPC G 01N 27/20. Appl. 27.11.2007, Publ. 27.06.2009, Bull. No 18.
4. V.M. Timokhin, V.M. Garmash, V.A. Tedzhetov, *Modern problems of science and education, No 3* (RAE: Moscow: 2013).
5. V.M. Timokhin, *Physics of dielectrics. Thermally activated and dielectric spectroscopy of crystalline materials. Proton transport* (Edition House "MISIS": Moscow: 2013).
6. E.V. Shpolsky, *Atomic physics, P. 1* (Nauka: Moscow: 1974) [in Russian].